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Sub-micron sized saccharide fibres *via* electrospinning

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Abstract: In this work, the production of continuous sub-micron diameter saccharide fibres is shown to be possible using the electrospinning process. The mechanism for the formation of electrospun polymer fibres is usually attributed to the physical entanglement of long molecular chains. The ability to electrospin continuous fibre from a low molecular weight saccharides was an unexpected phenomenon. The formation of sub-micron diameter "sugar syrup" fibres was observed *in situ* using high-speed video. The trajectory of the electrospun saccharide fibre was observed to follow that typical of electrospun polymers. Based on initial food grade glucose syrup tests, various solutions based on combinations of syrup components, i.e. mono-, di- and tri-saccharides, were investigated to map out materials and electrospinning conditions that would lead to the formation of fibre. This work demonstrated that sucrose exhibits the highest propensity for fibre formation during electrospinning amongst the various types of saccharide solutions studied. The possibility of electrospinning low molecular weight saccharides into sub-micron fibres has implications for the electrospinability of supramolecular polymers and other biomaterials.

Keywords: electrospinning; saccharides; carbohydrates

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1 Introduction

Electrospinning is a simple method for producing continuous polymer fibres with diameters in the sub-micron range [1–3]. During electrospinning a high voltage is applied to a small droplet of polymer solution (or melt), generating an electric field that stretches the droplet into a conical shape (*aka* the Taylor cone). The build-up of electrical charge due to the electric field overcomes the surface tension of the droplet, and a jet of polymer solution is emitted from the tip of the Taylor cone that may be collected at the nearest earthed object whereupon the jet is electrically discharged. The polymer solution is drawn into a fibre during flight if it has the appropriate electro-viscoelastic properties prior to reaching the collector [1, 3, 4].

The electrospinning of biopolymers such as chitosan polysaccharides [5–10], cellulose compounds [11–14], and proteins like collagen [15–18], zein [19–24], bovine serum albumin [25] and others [25–30] is well described in the literature. Electrospun polysaccharides [31, 32] and other bio-polymer based nanofibres show significant potential for a variety of biomedical applications [33–35] such as tissue engineering, wound dressing and cosmetics [15, 34, 36, 37]. While oligosaccharides and polysaccharides are known to form fibres by electrospinning [15, 31, 32, 38], the electrospinning of mono- or disaccharide-based solutions into fibres has not been reported yet. However, there are reports of the potential applications that low molecular weight saccharides could have in medicine, biology and microbiology [39] as well as in electrochemistry, and nanotechnology [40]. Hence, the electrospinning of saccharides could lead to the development of new devices for biosensing and drug-delivery [32, 38, 41, 42].

The present work demonstrates that short chain oligosaccharides (*e.g.* di-saccharides) are able to be electrospun into sub-micron sized fibres. Based on polymer chain entanglement theory, it has been postulated that at least 2.5 entanglements per chain are required in order for a polymer to form a continuous fibre during electrospinning (*i.e.* electrospinability) [43]. Hence, the present experimental findings are not consistent with the view that fibre

formation during electrospinning is inextricably linked to intermolecular chain entanglements [24, 43–45].

For example, when food grade polysaccharides were electrospun [15], it was found that highest Trouton ratios (the ratio of extensional viscosity to shear viscosity) corresponded to better electrospinability. This suggests that rheological elasticity (storage modulus > loss modulus) is an important property for the electrospinability of polysaccharides.

2 Experimental procedures

2.1 Materials

A culinary grade glucose syrup was used as received for the electrospinning experiments (Queen Fine Foods Ltd., Brisbane, Australia). The syrup is a glucose extract derived from corn that contains traces of sulfur dioxide (preservative 220) and sodium sulphite salts (80–150 mg/kg max). Mass spectrometry and high performance liquid chromatography confirmed that the syrup was mainly composed of monosaccharide (glucose and fructose ($C_6H_{12}O_6$)), disaccharide (sucrose and maltose ($C_{12}H_{22}O_{11}$)), and trisaccharide (raffinose ($C_{18}H_{32}O_{16}$)). Hence, a series of heterogeneous solutions using pure glucose (99.5%), sucrose (99.5%), fructose (99%), maltose (99%) and raffinose (98%) were synthesized to test its electrospinability. Materials were used as received from Sigma, without any modification.

2.2 Materials characterisation

2.2.1 High performance liquid chromatography

Sample preparation was carried out by dissolving a weighed amount of syrup in 1 mL of reverse osmosis-purified water [46]. After centrifugation at 14000 rev/min for 10 min, the supernatant was placed in a HPLC vial. Retention times and response factors generated by calibration standards of known sugars were used to identify and calculate concentrations of the unknown components [47, 48]. The concentrations were compared against three different points of the calibration curves for each sugar, and the results obtained had a coefficient of determination (r^2) close to unity (0.999). HPLC analysis was carried out using a Waters 2690 Pump, auto-sampler and Econosphere 5 micron amino column at 30°C. An isocratic mobile phase of 75.0% acetonitrile:water was used. Eluted sugars were detected using a Waters 2414 refractive index detector at 40°C.

2.2.2 Rheological properties

The rheological behaviour of the syrup was measured using an Anton-Paar MCR series rheometer (Anton Paar GmbH, Graz, Austria). All experiments were performed with a cone and plate geometry configuration (50 mm diameter) at a constant temperature of 50°C. The response of the syrup was measured in both rotational mode as a function of the shear rate (0.0001–100 s^{-1}) and oscillatory mode as function of the angular frequency (0.01–100 s^{-1}).

2.2.3 Preparation and characterization of electrospinning solutions

Solutions were prepared for electrospinning with a total saccharide concentration of 75 wt. % by dissolving the saccharide in de-ionised water at 50°C on a water bath controlled by a magnetic stirrer (Table 2). This concentration was chosen to ensure saccharide saturation of the solutions at the given experimental conditions. All saccharide solutions containers were tightly sealed since the start on the dilution process using the water bath, to minimize evaporation. Subsequently, all solutions were stored at 50°C due to a tendency for the saccharides to partially precipitate from a saturated solution at ambient temperature. An aqueous 75 wt. % raffinose solution exhibited precipitation at 50°C, hindering the electrospinning of this solution. Thus, an aqueous 65 wt. % raffinose solution (A3) was required to be prepared for the electrospinning experiments. All of the physical properties of the solutions were measured at 50°C to avoid precipitation of the saccharides.

Table 1: Aqueous saccharide solutions and designations.

Composition	Concentration	Sample code
Glucose	75 wt. %	A1
Fructose	75 wt. %	B1
Glucose/fructose	37.5 wt. % of each	C1
Sucrose	75 wt. %	A2
Maltose	75 wt. %	B2
Sucrose/maltose	37.5 wt. % of each	C2
Raffinose	65 wt. %	A3
Raffinose/sucrose/maltose	25 wt. % of each	B3
Raffinose/glucose/fructose	25 wt. % of each	C3

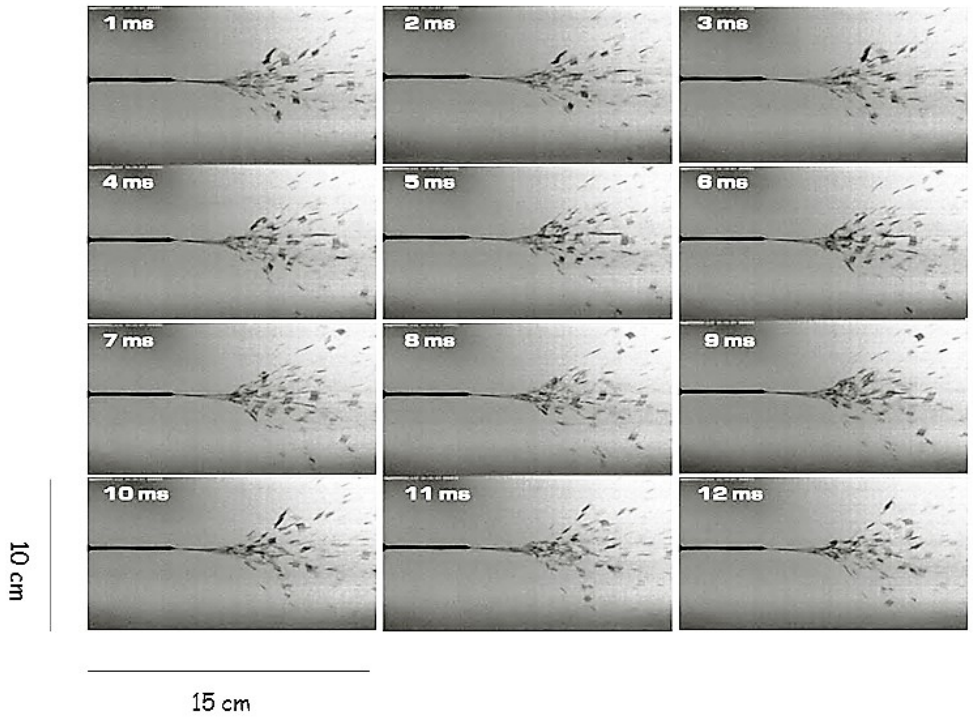

Figure 1: Series of high speed photographs taken at 1000 fps during the electrospinning of the glucose syrup.

The pH of the saccharide solutions was measured using a pH meter (SevenEasy, Mettler-Toledo GmbH, Greifensee, Switzerland). The surface tension was measured using a goniometer KSV CAM200 (KSV Instruments Ltd., Finland).

The electrical conductivity of the saccharide solutions was measured using a conductivity meter (EDT Instruments, RE387TX, Dover, United Kingdom). The pH, electrical conductivity and surface tension of the de-ionised water used in this work were 6.89, 8 μS/cm and 78 mM/m, respectively. All reported values are the averaged numbers based on three replicate measurements.

2.2.4 Electrospinning process and characterization of electrospun materials

A syringe pump (NE-500, New Era Pump Systems Inc., NY, USA) was used to deliver the electrospinning solution to the spinneret (metal hypodermic syringe needle, internal diameter of 0.3 mm) at a flow rate of 0.5 μl/min. All solutions were supplied to the spinneret, through a temperature controlled electric glass syringe cover, at a temperature of 50°C, (± 2°C) to avoid precipitation of the saccharides from solution. Electrospun samples were collected using a grounded aluminium foil substrate. The electrospinning apparatus was enclosed in a grounded Faraday cage. Electrospinning of the various solutions was performed using an applied voltage of +10 kV and a spinneret-to-collector distance of 15 cm (0.66 ± 0.03 kV/cm). The temperature and relative humidity within the set up were maintained at 30 ± 1°C and 35 ± 3%, respectively. The elevated ambient temperature was generated by the halogen lamps required for the high-speed photography. Electrospun samples were stored in a temperature-controlled desiccator at low ambient humidity prior to characterisation. A high-speed motion camera (MotionPro® X3) with sensitivity of 1280 × 1024 pixels was used for capturing photographic images of the jet during flight. The fibre in flight was illuminated by 6 × 12 V/50 W halogen lamps to provide consistent lighting conditions during video capture.

2.2.4.1 Microstructural analysis

The microstructure of electrospun samples was examined with scanning electron microscopy (JCM-5000 NeoScope, JEOL Ltd., Tokyo, Japan). Samples were directly observed without conductive coating necessary using secondary electron imaging at an accelerating voltage of 10 kV in high vacuum mode.

Table 2: Physical properties of the glucose syrup at 25°C.

Property	Value
Concentration	75% wt. % syrup/H_2O
Surface tension	98.11 mN/m
Conductivity	1.5 µS/cm
pH	5.5
Density	1.5 g/ml
Zero shear viscosity	38,600 Pa·s

3 Results and discussion

3.1 Glucose syrup properties

Typical electrospinability behaviour was observed for the glucose syrup, meaning stable and chaotic jet formation (see Figure 1). These photographs show the heaviest parts of the electrospun jet as dark beads, within the spinning cone. The polarity of the applied voltage did not influence the electrospinning behaviour of the glucose syrup, hence positive polarity was used throughout the experimentation. The glucose syrup was reduced to 75% wt. concentration, however its viscosity remained considerable high regardless of the dilution, see Table 2.

3.1.1 Glucose syrup processing

These results show for the first time that the glucose syrup, which actually contained a mixture of mono-, di- and trisaccharides, could form continuous filaments during electrospinning. The highly beaded structures of the filaments (see Figure 2C and 2D) clearly suggest a viscoelastic behaviour of the material during electrospinning. However, the high hydrophilicity of saccharides, does not promotes the stabilization of its fibrous structure for long periods of time, hence its flattened geometry, as shown on Figure 2A and 2B.

3.2 Glucose syrup characterization

3.2.1 Scanning Electron Microscopy

The syrup was analysed by mass spectrometry (MS) and high performance liquid chromatography (HPLC) to confirm the absence of starch or other polymeric materials. This, in order to eliminate the possibility that large polymeric molecules which may have been present on the syrup, were the responsible for fibre formation. However,

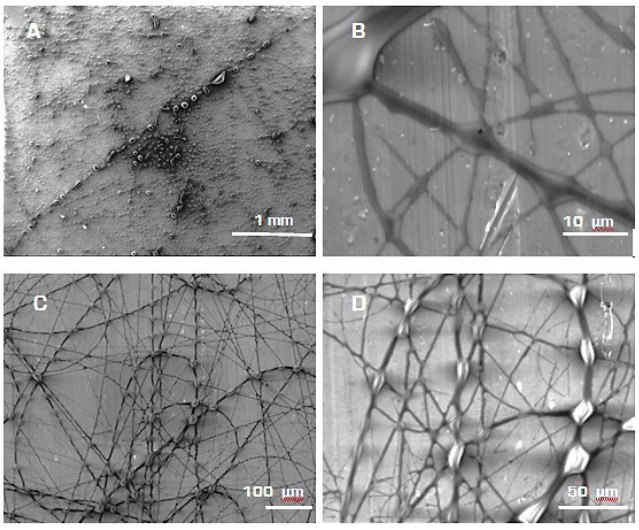

Figure 2: Four different samples of the electrospun glucose syrup at varying magnifications; as seen by the Scanning electron microscope. Area samples for the SEM analysis were chosen at random.

HPLC analysis indicated the presence of only the monosaccharides glucose and fructose, the disaccharide sucrose, and the trisaccharide raffinose, but no larger oligo- or polymeric structures (see Figure 4). Furthermore, MS confirmed the presence of these materials but provided no evidence of larger polymeric structures in the syrup (see Figure 3).

3.2.2 Mass – spectrometry

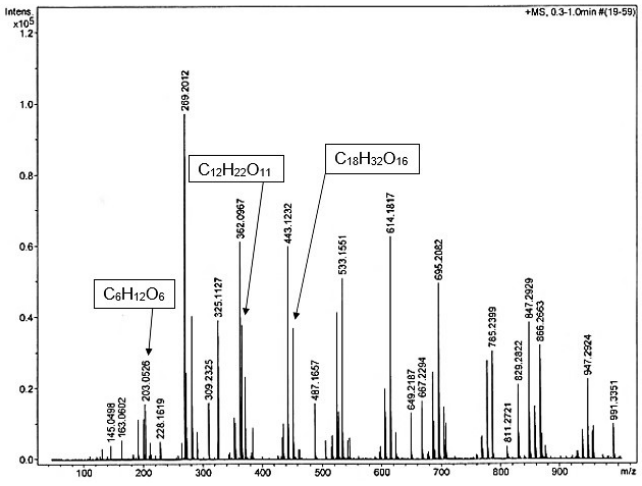

Figure 3: Mass spectrum from MS showing the intensity (y-axis) as a function of the mass-to-charge ratio (x-axis). The presence of the isomers of glucose, sucrose and raffinose are indicated at mass-to-charge ratios of 203.05, 365.1 and 527.16, respectively.

3.2.3 High Performance Liquid Chromatography

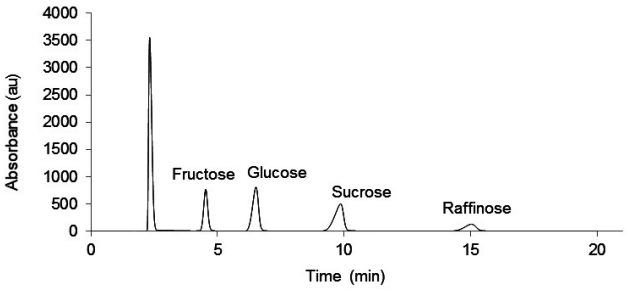

Figure 4: HPLC chromatogram confirming the presence of fructose, glucose, sucrose and raffinose in the glucose syrup. The first peak is the injection peak.

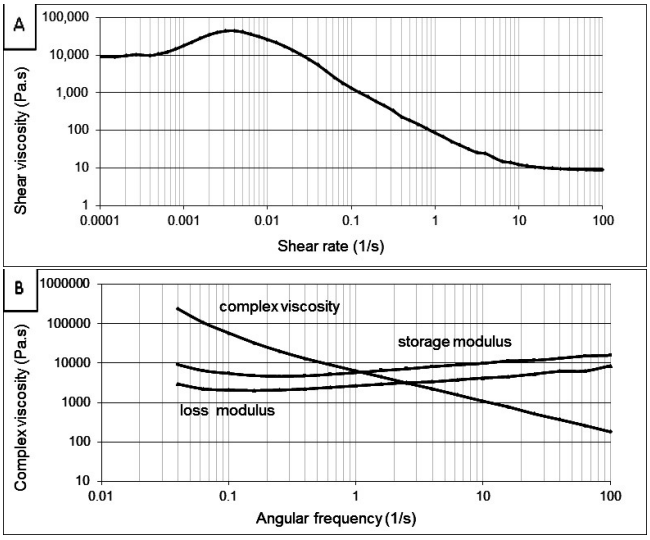

Figure 5: (A) shows the shear viscosity as a function of shear rate, (B) shows the complex viscosity, loss and storage modulus as a function of angular frequency of the glucose syrup.

3.2.4 Rheometry

Visco-elasto capillary theory sets different boundaries for spinnability depending on rheological properties as described by several non-dimensional numbers such as the Deborah number (De) and the Ohnesorge number (Oh), which should comply with the following electrospinnability condition De ≥ Oh ≥ 1 [49]. The Deborah number being the indicative of the relaxation time of the material to a given stress and the Ohnesorge number indicating the viscous response of a material to a given stress (or the inverse of a Reynolds number based on a characteristic capillary velocity) [49]. For Deborah numbers below unity, elastic effects do not stabilize the jet and Newtonian-like breakup dynamics are observed. For Ohnesorge numbers below unity, capillary wavelength instabilities are observed in the form of beaded filaments. However, the rheology results suggested that the glucose syrup performs as a polymer when mechanically stressed, since it showed a visco-elastic behaviour (see Figure 5A and 5B).

This apparent "viscoelasticity" agrees in principle with the visco-elasto-capillary thinning theory for complex fluids as described by McKinley [49]. Since the shear thinning response of the viscosity measurements (Figure 5A), indicates the initial viscous response of the solution to an increasing shear rate, followed by an elastic thinning response as indicated by a decreasing shear viscosity (slope) beyond a shear rate of ~0.01 s^{-1} [50, 51]. However, the frequency response of the storage and loss modulus of the syrup shows that this behaviour is mostly elastic [52], since the storage modulus is greater than the loss modulus over the entire frequency range measured (Figure 5B). This further supports the evidence that higher Trouton ratios corresponded to better electrospinability (storage modulus > loss modulus) [15].

3.3 Saccharide solutions characterization

3.3.1 Microstructural Analysis (SEM)

It is evident from Figures 6 and 7 that neither the monosaccharides glucose or fructose, nor the trisaccharide raffi-

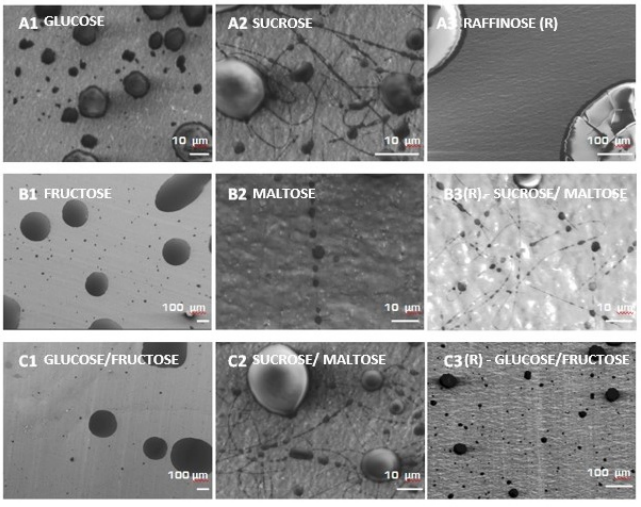

Figure 6: Representative scanning electron micrographs of the electrospun solutions. Images are presented at different magnifications to aid structure visualization.

nose, nor their combinations, were able to form fibres *via* the electrospinning process. In contrast, the disaccharides sucrose and maltose, and combinations of them, gave more continuous filament formation (see Figure 6 – A2, C2 & B3). For solutions series 1(ABC) as well as for A3 and C3, no electrospinning or electrospun fibre formation was observed, rather only an emission of droplets (electrospray).

3.3.2 High speed photography and microstructural Analysis

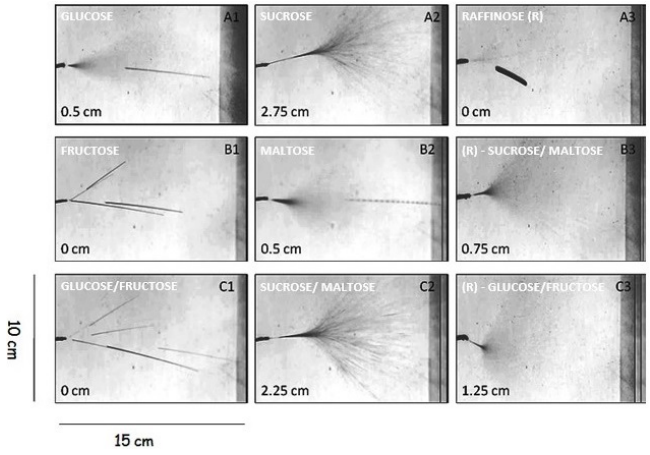

Figure 7: Representative photographs of the electrospinning behaviour of each solution showing the length of the stable jet.

3.3.3 Saccharide solutions properties

Figures 8 and 9 show that sucrose (A2), the material with better electrospinnability - highest amount of continuous filament formation, had the lowest conductivity and the highest pH. This observation seems counter-intuitive according to some reports on polymer electrospinnability [53–55], wherein the ionic conductivity can be an important parameter for the electrospinnability of polymers, since an increment in the conductivity relates to an increment in the amount or capacity of the charge carriers (ions), and therefore better charge mobility or conductivity [56–59].

However, the fact that sucrose had the lowest surface tension is in agreement with visco-elasto capillary theory, which states that an electrospinnable system will tend to minimise its total boundary energy (effectively its surface tension) to form continuous filaments [43, 45, 60].

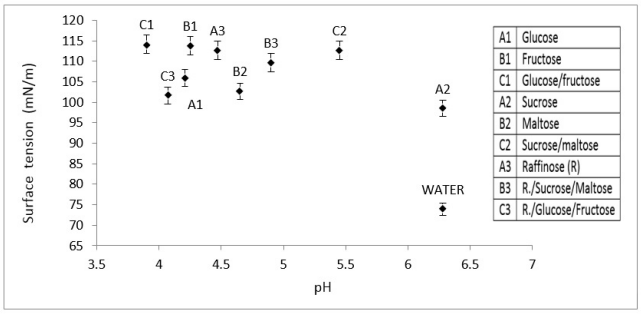

Figure 8: Surface tension as a function of pH. All measurements were taken at 50°C ± 3.5°C.

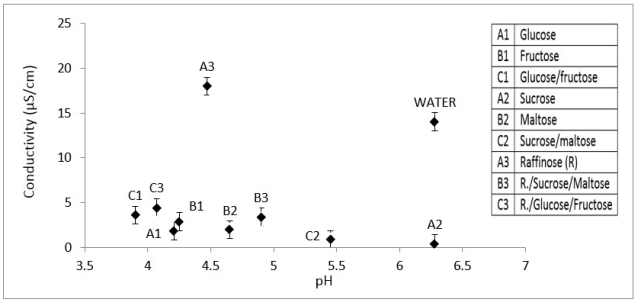

Figure 9: Electrical conductivity as a function of pH. All measurements were taken at 50°C ± 3.5°C.

Nonetheless, it is not clear how intermolecular hydrogen bonding systems, for example concentrated saccharide solutions, could play a role in the cohesive surface energy during electrospinning [61, 62].

3.4 Syrup replica

To further confirm the electrospinnability of the commercially supplied glucose syrup, a duplicate solution was made up by combining the pure components that had been previously identified by HPLC, at similar relative concentrations of each material. Namely glucose (34 wt. %), fructose (22.5 wt. %), sucrose (32 wt. %), and raffinose (11.5 wt. %) in distilled water, to give a final total solids concentration of 85 wt. %.

3.4.1 Syrup replica - microstructural analysis (SEM)

The fact that this solution exhibited similar behaviour to the commercially supplied glucose syrup (*i.e.* produced continuous filamentation), provided strong evidence that the presence of polymeric materials, which might have been present but were not detected by HPLC or MS, was

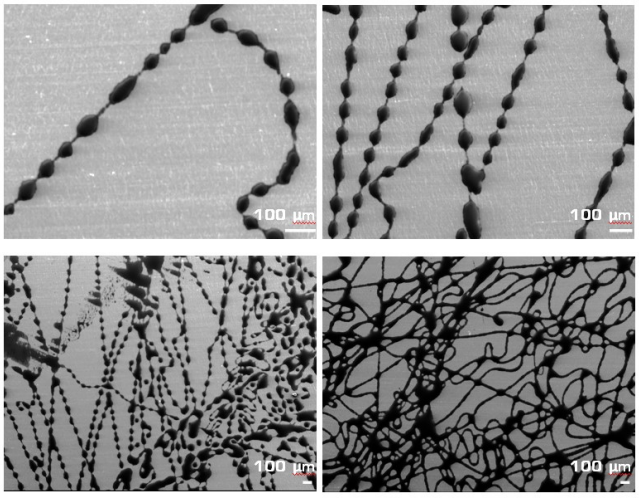

Figure 10: Scanning Electron Microscope (SEM) images of fibres made from the duplicate of the glucose syrup.

not a requirement for electrospinability. The observations of this study therefore do not fit into the frameworks of either chain entanglement [43] and suggest that alternative mechanisms are involved in the production of saccharide electrospun fibres.

4 Conclusions

These results show for the first time that a heterogeneous mixture containing mono-, di- and tri- saccharides can form continuous filaments during electrospinning, and can exhibit the same behaviour as polymeric solutions whilst being electrospun; namely the formation of a stable jet followed by whipping instability.

From the rheology analysis it is suggested that storage modulus > loss modulus could be the cause for the apparent elasticity of the material, allowing for the unusual stretching of the stable electrospun jet. Furthermore, the surface tension data for sucrose agrees with elastocapillary theory i.e. that "an electrospinnable system will tend to minimize its superficial energy to form continuous filaments" [49, 52, 56, 63]. Remarkably, the electrospinnability of all these materials is not consistent with current proposed chain entanglement [43] theory of electrospinning.

Conclusively, chain entanglement theory does not adequately describes the electrospinning behaviour of saccharides, which exhibited non-linear viscoelasticity and complex charge transfer mechanisms due to their extensive intermolecular bonding [42].

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